

Calculating the hydrogen molecule ion using the two particle Schrödinger equation

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We calculate the hydrogen molecule ion from the two particle Schrödinger equation. Therefore a very simple two particle basis set is chosen. We suggest this ansatz to be used to solve the "two electron one phonon" three particle wave-function of a BCS superconductor. Possibly it can give hints for high temperature superconductors.

I. INTRODUCTION

Quantum mechanical calculations of rotational, vibrational and electronic excitations in molecules are usually done in the Born Oppenheimer approximation [1]. The electron-phonon system of crystals is usually calculated in this approximation, too. Coupling of vibrations and electronic excitations is calculated due to perturbation theory. In this article we take the hydrogen molecule ion as a very simple example of a system with rotational, vibrational and electronic excitations and suggest a way of calculating it without using the Born Oppenheimer approximation. Therefore we will use two particle wave-functions. The same concept may be used to calculate electron-phonon systems of crystals.

II. CALCULATION

We use the Schrödinger equation

$$H|\varphi\rangle = e|\varphi\rangle \quad (1)$$

for the hydrogen molecule ion. The problem has three particles, but it can be reduced to a two particle problem in a similar way, as the hydrogen atom can be reduced from a two particle problem to a one particle problem [1]. The Hamiltonian has the form

$$H = -\frac{\hbar}{2m_a}\Delta_a - \frac{\hbar}{2m_b}\Delta_b - \frac{\hbar}{2m_c}\Delta_c + \frac{e_a e_b}{|\vec{r}_a - \vec{r}_b|} + \frac{e_b e_c}{|\vec{r}_b - \vec{r}_c|} + \frac{e_a e_c}{|\vec{r}_a - \vec{r}_c|}. \quad (2)$$

Δ_a , Δ_b and Δ_c are the Laplace operators with respect to the positions of the particles \vec{r}_a , \vec{r}_b and \vec{r}_c , respectively. We introduce the center of mass

$$\vec{R} = \frac{m_a \vec{r}_a + m_b \vec{r}_b + m_c \vec{r}_c}{m_a + m_b + m_c} \quad (3)$$

and get new variables

$$\vec{r}_a = \vec{r}_1 + \vec{R}, \quad \vec{r}_b = \vec{r}_2 + \vec{R}, \quad (4)$$

$$\vec{r}_c = -\frac{m_a \vec{r}_a + m_b \vec{r}_b}{m_c} = -\frac{m_a(\vec{r}_1 + \vec{R}) + m_b(\vec{r}_2 + \vec{R})}{m_c}. \quad (5)$$

We are only interested in solutions, which do not depend on the motion of the center of mass, therefore we use $\vec{R} = 0$

$$\vec{r}_a = \vec{r}_1, \quad \vec{r}_b = \vec{r}_2, \quad \vec{r}_c = -\frac{m_a \vec{r}_1 + m_b \vec{r}_2}{m_c}. \quad (6)$$

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Let $m_a = m_e$ be the electron mass, $m_b = m_c = m_p$ be the proton mass, $e_a = -e$ the electron charge and $e_b = e_c = e$ the proton charge. With $m_a \ll m_c$ and $m_b = m_c$ we get

$$\vec{r}_c = -\vec{r}_2. \quad (7)$$

This is not a Born Oppenheimer approximation, it is just a simplification of the calculation. The value of r_c can be wrong by 0.0005 of usual distances in the hydrogen molecule ion. Within our calculation of the matrix elements this will be a small error with respect to the integration errors from Monte-Carlo integration.

Using the new variables \vec{r}_1 and \vec{r}_2 we get a two particle Hamiltonian

$$H = -\frac{\hbar}{2m_e}\Delta_1 - \frac{\hbar}{4m_p}\Delta_2 + \frac{e^2}{2|\vec{r}_2|} - \frac{e^2}{|\vec{r}_1 + \vec{r}_2|} - \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}. \quad (8)$$

Δ_1, Δ_2 are the Laplace operators with respect to \vec{r}_1 and \vec{r}_2 , respectively. Due to constrains the mass moved by changing \vec{r}_2 is $2m_p$. With this Hamiltonian we calculate the matrix elements for the Schrödinger equation for a chosen two particle basis-function set. We use the linear combination ansatz and the variation theorem

$$\varphi(\vec{r}_1, \vec{r}_2) = \sum_i c_i \varphi_i(\vec{r}_1, \vec{r}_2). \quad (9)$$

From the expectation value e of the energy

$$\langle \varphi | H | \varphi \rangle = e \langle \varphi | \varphi \rangle, \quad (10)$$

we get

$$\int dV_1 dV_2 \sum_{ij} c_j \varphi_j^*(\vec{r}_1, \vec{r}_2) H c_i \varphi_i(\vec{r}_1, \vec{r}_2) = \int dV_1 dV_2 \sum_{ij} c_j \varphi_j^*(\vec{r}_1, \vec{r}_2) e c_i \varphi_i(\vec{r}_1, \vec{r}_2), \quad (11)$$

and write it as

$$\sum_{ij} c_j H_{ij} c_i = e \sum_{ij} c_j S_{ij} c_i \quad (12)$$

with

$$H_{ij} = \int dV_1 dV_2 \varphi_i H \varphi_j, \quad S_{ij} = \int dV_1 dV_2 \varphi_i \varphi_j. \quad (13)$$

The integrals must be calculated over two 3D-volumes, as φ_i are two particle basis-functions. From the variation theorem the energy e is a minimum with respect to all parameters c_j

$$\frac{\partial}{\partial c_j} \frac{\sum_{ij} c_j H_{ij} c_i}{\sum_{ij} c_j S_{ij} c_i} = 0. \quad (14)$$

With this ansatz the Schrödinger equation looks like

$$\sum_i H_{ij} c_i = e \sum_i S_{ij} c_i. \quad (15)$$

This is a general eigenvalue problem which can be solved numerically. Also the integrals H_{ij} and S_{ij} can be solved numerically, for example by Monte Carlo integration.

III. BASIS-FUNCTIONS FOR SOLVING THE TWO PARTICLE SCHRÖDINGER EQUATION

The choice of the two particle basis-functions $\varphi_i(\vec{r}_1, \vec{r}_2)$ will be evaluated now. If two particle electron wave-functions are needed, often the ansatz $\varphi_{pq}(\vec{r}_1, \vec{r}_2) = \psi'_p(\vec{r}_1) \phi'_q(\vec{r}_2)$ is used. In our case this ansatz will be very bad, because one particle is a (quasi) proton, the other an electron. The motion of the electron is not independent from the motion of the protons, as the electrons will have highest probability density near the protons. A simple approach could be

$$\varphi_{pq}(\vec{r}_1, \vec{r}_2) = k_{pq} \psi_p(\vec{r}_1) (\phi_q(\vec{r}_2 - \vec{r}_1) + s \phi_q(\vec{r}_2 + \vec{r}_1)). \quad (16)$$

Eigenvalue [a.u.]	c_{00}	c_{10}	c_{20}	c_{30}
-0.521112	-0.99955	0	-0.0299897	0
-0.520852	0	-0.999777	0	-0.0211105
-0.505818	-0.198128	0	0.980176	0
-0.505597	0	0.190136	0	-0.981758

Table I: Results of sample calculation

We will use ψ_p and ϕ_q as radial symmetric functions. The combination of the indices p and q correspond to the index $i \rightarrow pq$ in (15). k_{pq} is the normalization constant and will be calculated from the overlap integrals $\int dV_1 dV_2 \varphi_{pq} \varphi_{pq} = 1$. $(\phi_q(\vec{r}_2 - \vec{r}_1) + s\phi_q(\vec{r}_2 + \vec{r}_1))$ describes the electron part of the basis-functions. The highest probability density of the electron is near both protons. s is $+1$ or -1 characterizing the bonding and anti-bonding wave-functions of the electron [1]. We will only use $s = 1$ for bonding wave-functions and use simple basis-functions for ϕ_q and ψ_p

$$\begin{aligned}\psi_p(\vec{r}) &= f_p(\vec{r})e^{-w_{proton}(|\vec{r}| - r_0)^2}, \\ \phi_0(\vec{r}) &= e^{-w_{electron}(|\vec{r}|)^2}.\end{aligned}\tag{17}$$

r_0 is the half of the proton-proton distance. As functions f_p we use:

$$f_0(\vec{r}) = 1, \quad f_1(\vec{r}) = \frac{x}{|\vec{r}|}, \quad f_2(\vec{r}) = (|\vec{r}| - r_0), \quad f_3(\vec{r}) = f_2(\vec{r})f_1(\vec{r}),$$

$$\text{with } \vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}.\tag{18}$$

ψ_0 should be similar to the wave-function for $l = 0, n = 0$ (rotational and vibrational ground stage), ψ_1 is similar to $l = 1, n = 0$, ψ_2 is similar to $l = 0, n = 1$, ψ_3 is similar to $l = 1, n = 1$. ψ_0 is constructed as ground wave-function of a harmonic oscillator, ψ_2 is the first excitation of a harmonic oscillator with respect to the radial dependency (r_0 is the mean distance of the protons from the center of mass) [1]. $f_1(\vec{r})$ describes the spheric harmonics for $l = 1$. $\phi_0(\vec{r})$ is a Gaussian type ground wave-function for the electron. With this basis-functions we choose approximate parameters in atomic units

$$\begin{aligned}w_{proton} &= 18, \\ w_{electron} &= 0.45, \\ r_0 &= 1.0.\end{aligned}\tag{19}$$

This parameters can be calculated by searching the minimum of the ground state energy from equation (15) with respect to w_{proton} , $w_{electron}$ and r_0 . This is not done within this article, as the computational power was not available. We only did some test calculations to check, if we are near the minimum. The parameters are taken from known properties of the hydrogen molecule ion [2].

The results for the four eigenvalues and eigenvectors are shown in table I. They are not very good compared to other calculations, but of cause the choice of the basis set is very simple. The ground state wave-function is close to φ_{00} , the first excitation is the rotational excitation with a wave-function close to φ_{10} . The second excitation is the vibrational excitation with a wave-function close to φ_{20} . The calculated energy for the first rotational excitation is $0.00026 \text{ a.u.} = 0.007 \text{ eV}$. The calculated energy for the first vibrational excitation is $0.0153 \text{ a.u.} = 0.41 \text{ eV}$. The values can be compared to literature [2]. The energy of the vibrational excitation is calculated to high. The literature value is about 0.27 eV . One can see from table I, that the eigenfunctions are not very good. In the linear combination also c_{00} differs from zero.

IV. DISCUSSION

The suggested basis-functions (16) can be used to calculate the two particle problem of the hydrogen molecule ion. As result we get two particle wave-functions for the ground state, the first rotational excitation and the first vibrational excitation.

The chosen basis-functions are very simple functions and the basis set is very small. They can of course be improved in a number of ways. Especially for the electron part of the wave-function we did not even include basis-functions for electronic excitations.

Additionally the separation (equation: 16) does not allow electron phonon interaction, as the electron wave-function does not depend on the protons. One will need electron basis-functions, which include the proton-proton distance $2|\vec{r}_2|$ to include electron-phonon interaction. This is not a principle problem, as the separation is only used to construct simple basis-functions. The separation is not needed for the calculation in any way. With enough computational power it should be possible to use a subset of a complete set of basis-functions. With the use of such a subset, no artificial approximations are needed to solve the Schrödinger equation and the precision can be increased by increasing the number of basis-functions in the subset.

V. OUTLOOK

This ansatz can be transferred to crystal lattices. The aim would be to calculate the electron-phonon system in a one electron, one phonon (more general: vibrational excitation) approximation ab initio. In a next step a "two electron one phonon" approximation could be used to calculate the electron-phonon system of a BCS superconductor. With the choice of a subset of a complete set of three particle basis-functions no additional approximations will be needed (but the limited number of basis-functions in the subset). It would be quite interesting to see, how this wave-functions look like.

Possibly this ansatz can give new ideas, how to describe high temperature superconductors.

VI. RESOURCES

The source code of this calculation is available [3]. Please contact the author in case you want to work on the topic.

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- [1] Landau Lifschitz, Theoretische Physik III, Quantenmechanik, Akademie-Verlag Berlin.
 - [2] Dr. Randell L. Mills, The Grand Unified Theory of Classical Quantum Mechanics, ISBN 0963517163, <http://www.blacklightpower.com/bookdownload.shtml>
 - [3] <http://www.physik.de/tp/source.html>